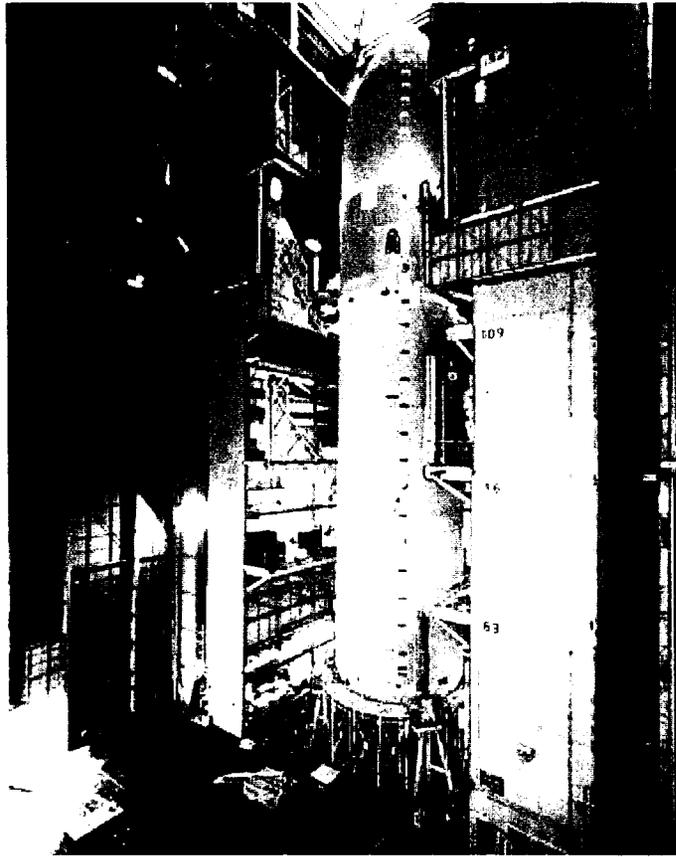


## SPACE SHUTTLE PROGRAM PETITION FOR HCFC 141b Exemption Allowance



*Figure 3.2 Completed ET in Spray Cell*

The third spray foam is used on the forward LH<sub>2</sub> dome and the aft LO<sub>2</sub> dome using an automated process similar to that used with the major acreage foam sprays. It is also sprayed manually in closeout applications (in which foam is applied after an assembly or part has been installed), on small components, and for repairs. As with the high-index isocyanurate foams, the mixed foam material undergoes an exothermic chemical reaction resulting in the boiling of the blowing agent, and within seconds of application hardens to a solid foam. Successive layers are sprayed onto the substrate until the desired thickness is obtained. After curing, the foam is machined to the final dimensions as required by the engineering design.

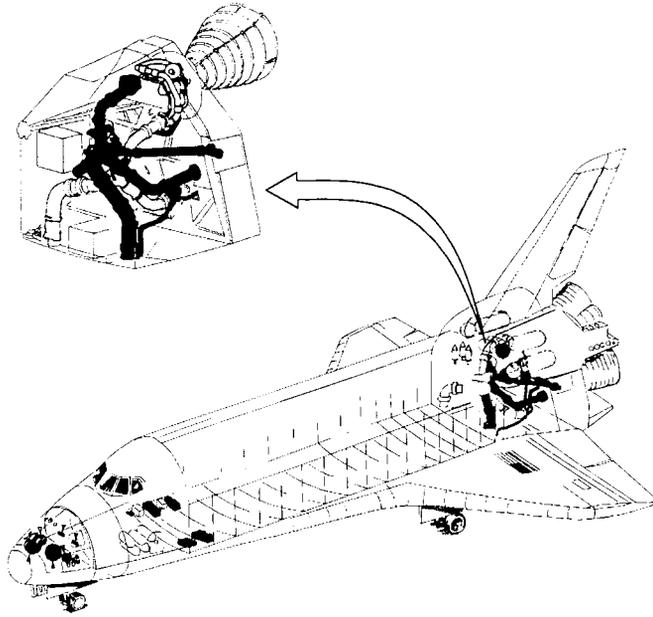
The fourth foam is supplied as a two-component liquid system that is manually mixed and hand applied. It is used to make small repairs and closeout small areas.

In order for the vehicle aerodynamic loads to be calculated for the foam covered parts it is essential for the foam to be dimensionally stable for all prelaunch temperature and moisture conditions and for all flight conditions. The final, post-machining dimensions are documented in a "Moldline and Protuberance Interface Control Document."

### **3.2 ORBITER USES OF HCFC 141b BLOWN FOAM**

Orbiter uses HCFC 141b blown foam to thermally insulate the Main Propulsion System (MPS) and Power Reactant Storage and Distribution (PRSD) hardware. The MPS and PRSD, shown in Figure 3.3, are two of the Orbiter's most important and critical subsystems. A more detailed description of the primary elements of the Shuttle Orbiter, MPS, and PRSD as well as their function is given in Appendix A.

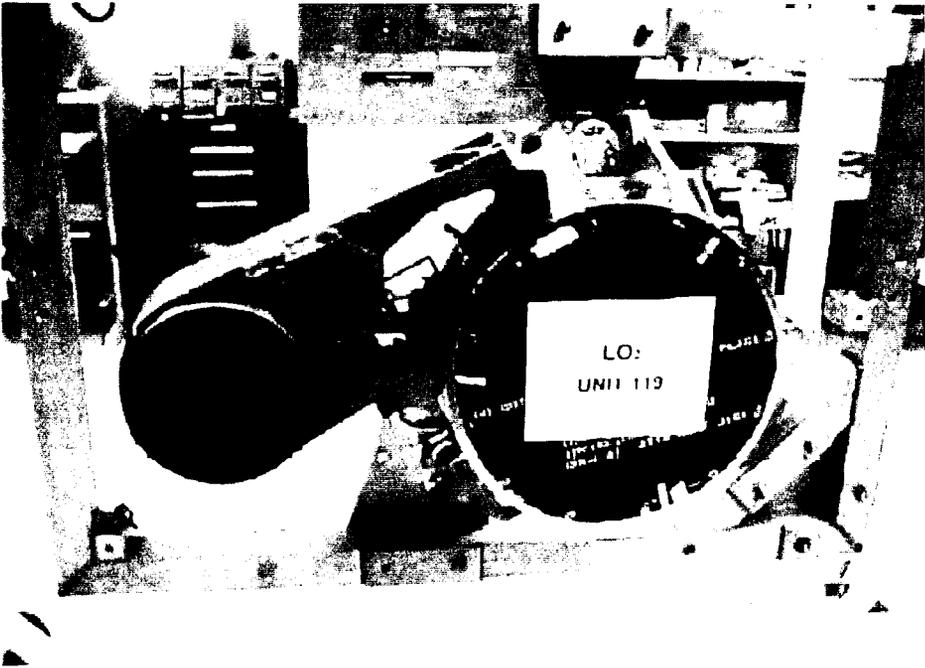
## SPACE SHUTTLE PROGRAM PETITION FOR HCFC 141b Exemption Allowance



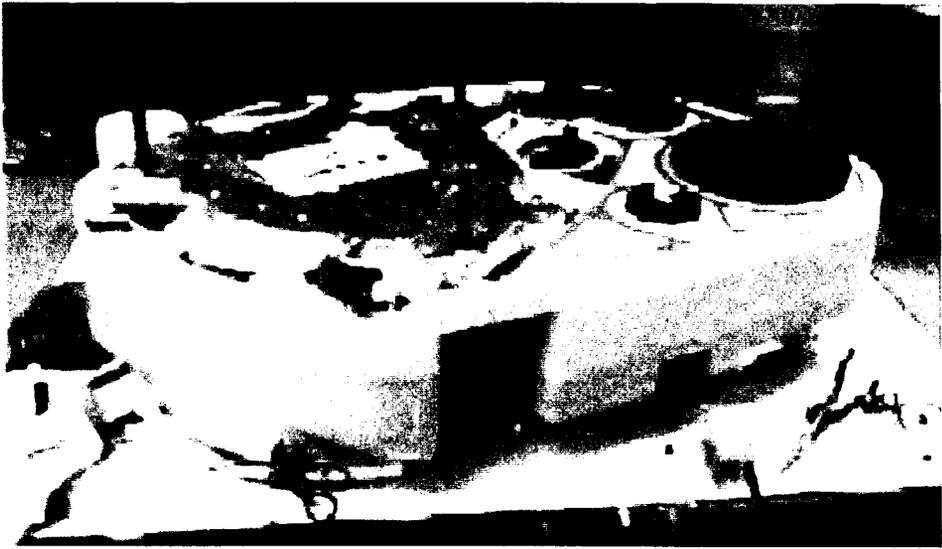
*Figure 3.3 Orbiter Use of HCFC Foam*

The MPS is critical because it provides propulsion for Orbiter from liftoff to the moment that it enters earth orbit. HCFC 141b foam is used on nearly 40 MPS components. These parts include liquid hydrogen and liquid oxygen flanges, prevalves, disconnects, umbilicals and others, which are critical for proper propellant transfer to Shuttle main engines. A good example of an MPS foam application is the umbilical connecting the ET to the Orbiter. Cryogenic propellants flow between the tank and Orbiter at this critical location, necessitating the use of HCFC 141b blown foam insulation. Figures 3.4 and 3.5, respectively, illustrate the umbilical without and with foam insulation.

SPACE SHUTTLE PROGRAM PETITION FOR HCFC 141b Exemption Allowance



*Figure 3.4 Seventeen-Inch Umbilical Prior to Application of HCFC 141b Foam*



*Figure 3.5 Seventeen-Inch Umbilical After Application of HCFC 141b Foam*

## **SPACE SHUTTLE PROGRAM PETITION FOR HCFC 141b Exemption Allowance**

The umbilical disconnects are foamed in a closed mold using an HCFC 141b blown closed cell rigid polyurethane foam system. This foaming operation is performed at Palmdale, California. This mold is a multi-component glass laminate that encapsulates the entire exterior surface of the umbilical disconnect. The HCFC 141b blown foam is supplied in 5-gallon (19-liter) kits as a two-component liquid system. The material is hand-mixed and molded prior to application.

Similarly, the flanges and pre-valves are foamed in closed molds using an HCFC 141b blown foam system. This foaming operation is performed either at Palmdale, California or at KSC.

Foam blown with HCFC 141b prevents the formation of gas in the liquid propellant lines by insulating these lines from heat. If the foam does not have the required thermal conductivity, the lines will no longer be insulated from external heat and liquid fuel will vaporize into gas. This vaporized liquid fuel will disrupt critical flow of propellant from the External Tank to the main engines of the Shuttle Orbiter. Because the engines are set to run at a predetermined rate of propellant flow, if propellant starts heating up and flow is impacted by the formation of gaseous propellant, the engines will no longer function properly. This scenario would quickly lead to mission deterioration and endangerment of crew.

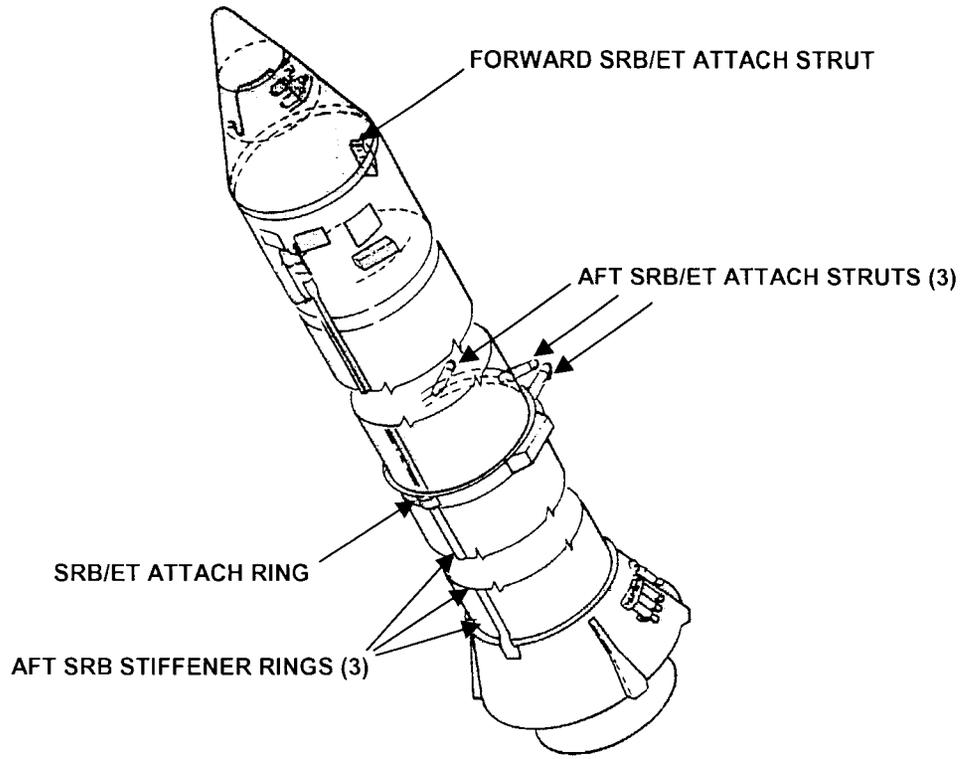
The PRSD stores hydrogen and oxygen for distribution to three fuel cells providing electrical power production. PRSD also distributes oxygen for crew respiration and is vital for Orbiter performance and safety. HCFC 141b foam is used on approximately 20 PRSD components. Most of these parts are feedlines that carry liquid hydrogen or liquid oxygen. It is critical that these lines remain well insulated for cryogenic liquid flow to distribution systems. The PRSD feed-lines are also foam-insulated under the same environmentally controlled conditions. The finished foam is machine-milled to remove excess foam, then installed on the feed-lines.

### **3.3 SRB USES OF HCFC 141b BLOWN FOAM**

In the assembled Space Shuttle system, the two SRBs are mounted on either side of the ET. The boosters are each 149.1 feet (45.45 meters) high and 12.2 feet (3.72 meters) in diameter. Each booster weighs 700 tons (635,000 kilograms) and produces 2,658,000 pounds (11,800,000 newtons) of thrust at liftoff, providing nozzle gimbal authority for thrust vector control. Together, the SRB flight pair accelerates the vehicle to 3,000 miles (4,800 kilometers) per hour, then separates from the vehicle at an altitude of approximately 27 nautical miles. After separation, the boosters parachute into the ocean and are towed back to KSC where they are refurbished for another mission.

SRB components requiring HCFC 141b foam application are the SRB/ET Attach Ring, Solid Rocket Motor Stiffener Rings, and SRB/ET Attach Bolt Catchers. Figure 3.6 illustrates SRB locations of HCFC 141b foam applications.

## SPACE SHUTTLE PROGRAM PETITION FOR HCFC 141b Exemption Allowance



*Figure 3.6 Space Shuttle Solid Rocket Booster*

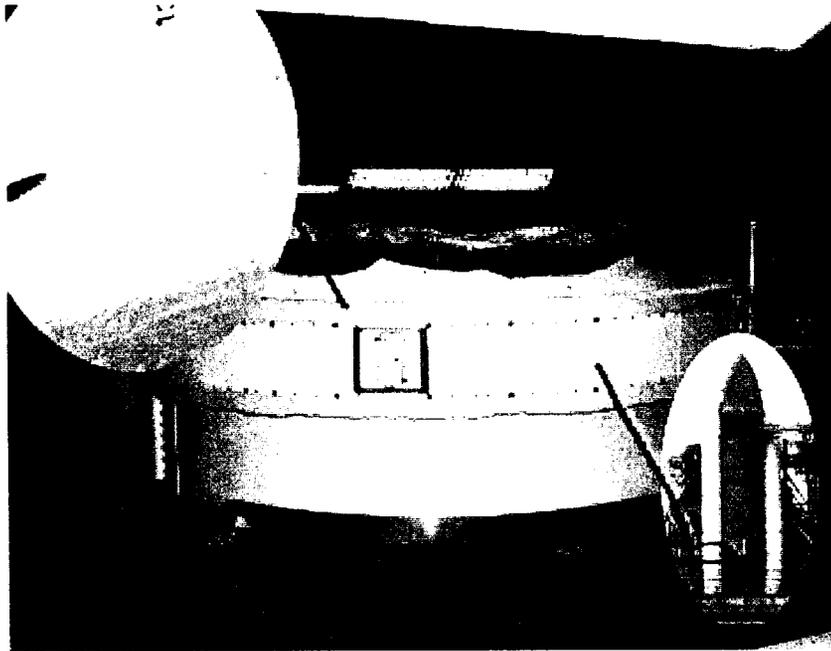
The Attach Ring (Figure 3.7) is a 360° segment located one-third the way up the booster. This ring is one of the load bearing structures that transfer the propulsive force from the SRB to the ET. The aft motor segment has three steel Stiffener Rings (Figure 3.8) to protect the metal motor casing during booster splashdown. Foam is used in these areas for ascent thermal protection and to absorb descent splashdown loads. HCFC 141b pour foam is used to repair areas in the acreage foam on both the Attach Ring and the steel Stiffener Rings.

There are three aft strut assemblies connecting each SRB to the ET. These struts act to dampen ET/Orbiter loads borne by the SRBs. Within each assembly, explosive charges shear the connecting shaft inside the strut during SRB/ET separation after launch. After shearing, the connecting shafts, or "bolts" are captured by the HCFC 141b pour foam and an aluminum honeycomb structure within the bolt catchers. The Aft Attach Struts are shown in Figure 3.6.

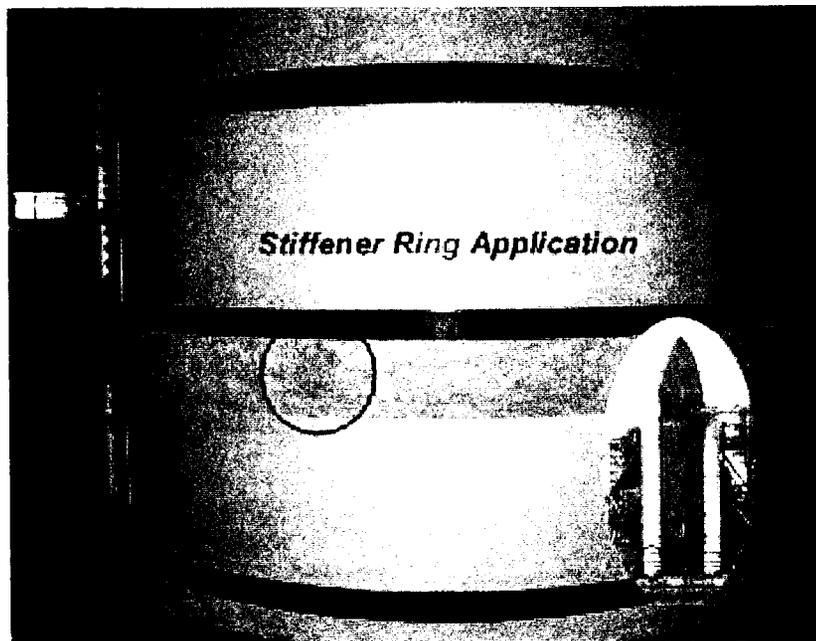
The Forward Skirt Assembly houses an attach fitting (see Figure 3.6) that transfers the SRB thrust loads to the ET. An explosive charge separates the SRBs from the ET by shearing connecting bolts that are captured by bolt catchers similar to those associated with the Aft Attach Struts.

A manually mixed HCFC 141b pour foam is used to make small repairs and close out small areas. This foam is supplied as a two-component liquid system.

SPACE SHUTTLE PROGRAM PETITION FOR HCFC 141b Exemption Allowance



*Figure 3.7 ET Attach Ring*



*Figure 3.8 Steel Stiffener Ring*

# SPACE SHUTTLE PROGRAM PETITION FOR HCFC 141b Exemption Allowance

## 4.0 EVALUATION OF HCFC 141B ALTERNATIVES

Human space flight safety is of paramount importance to NASA. It is critical to recognize the necessity of demonstrated reliability in the SSP. The Space Shuttle is a human-rated flight vehicle and introduction of new materials jeopardizes proven reliability. Prior to implementation on the Shuttle system, a new material must undergo a rigorous development and qualification program. This section discusses the steps that must be taken to implement a new material on the Space Shuttle, and specifically those that have been taken to find next generation alternatives to HCFC 141b as the blowing agent for the Space Shuttle foam thermal protection systems. The SSP is constrained by flight safety and performance requirements.

### 4.1 IMPLEMENTATION ISSUES FOR FOAM SYSTEMS

#### 4.1.1 Foam Development and Qualification Process

Prior to implementation on the Space Shuttle, a new material must undergo a rigorous development and qualification program. The SSP approach to evaluating blowing agents is composed of steps illustrated in Figure 4.1.

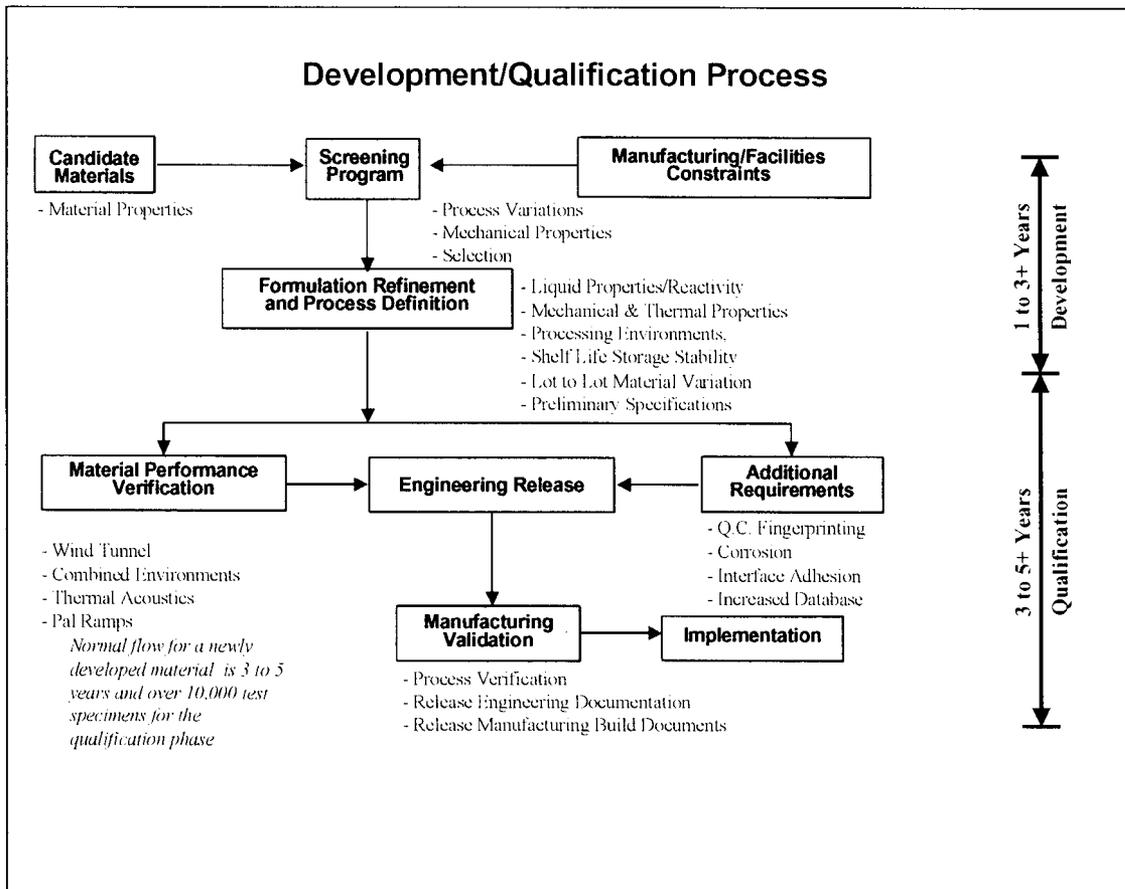


Figure 4.1 Foam Development and Qualification Process

The first step in this process is to screen potential materials and select likely candidates based on material properties and their compatibility with manufacturing and facilities constraints. Certain criteria are used for selection of a new blowing agent that can be used to make SSP foam insulation. Materials are sought that are

## SPACE SHUTTLE PROGRAM PETITION FOR HCFC 141b Exemption Allowance

soluble in isocyanate and polyol components of urethane insulators; possess low toxicity, with supporting data from toxicity tests; have a boiling point range of 77°F (25°C) – 113°F (45°C); EPA-approved, preferably zero ozone depletion potential (ODP) and minimal global warming potential; and are commercially available. Process variations and mechanical properties are evaluated in the selection process. Formulation refinement and process definition include assessment of liquid properties/reactivity, mechanical and thermal properties, processing environments, shelf life storage stability, and lot-to-lot material variation. Preliminary specifications are also established at this time. SSP foams must be sufficiently robust to survive manufacturing and transportation activities. Foam components must have a shelf life stability of one year. Both foam components and formulated foams must be able to maintain lot-to-lot manufacturing consistency. Process control must be maintained within defined manufacturing constraints to assure material repeatability and meet predictable flight performance requirements. Development is an iterative process involving several blowing agent candidates and various foam formulations.

Once a candidate is selected, the qualification phase begins. This phase greatly expands testing of the new foam system to include processing variations, lot-to-lot variability, shelf life, manufacturing capability, and design verification testing using various lots of material. Wind tunnel, cryogenic strain, radiant heating, physical property, density, and thermal conductivity materials tests are performed on potential foam systems.

Development of an extensive database is required before a product is ready for implementation on manned space flight hardware. The blowing agent used in a foam material can significantly affect any or all of the foam properties. A significant amount of development and qualification testing must be performed to ensure that the material meets all of the requirements for mission success and human flight safety.

Certain tests have been identified as critical requirements for each material. These tests are for mechanical properties (tensile and compressive strength), physical properties (density, thermal conductivity, and dimensional stability), cryostrains (to -423°F (-253°C)), and ablative recession (aero and radiant heating). Test samples/specimens are obtained from foam-insulated panels that are processed to meet engineering or flight requirements and represent actual manufacturing conditions. Upon successful completion of the above tests, the foam material must be validated in the manufacturing process before implementation.

### 4.1.2 Other Issues

The ET's transition from CFC 11 blown foams to HCFC 141b foams required eight years to complete and was not without unanticipated program impacts. The development and qualification effort was more extensive than anticipated and, once validated, processing difficulties led to an increase in labor hours for application. The large acreage foam was much more difficult to process than its predecessor because it caused a build up in the spray guns. Eventually multiple guns had to be added to the process to solve the problem. A reduction in compressive and tensile strengths was also realized due to the change from CFC 11 blown foam.

Despite many developmental tests and flight simulation test articles during the replacement of the class I ODC foams with HCFC 141b foams, it was discovered, only after flight, that the new materials exhibited performance issues in some applications. The new foams were also more susceptible to a phenomenon known as "popcorning", sporadic loss of small pieces of foam at low heating rates, leading to ET Intertank foam loss that ultimately resulted in Orbiter TPS tile damage. If foam debonds and falls off, it can impact or contaminate another area where it may cause damage. It should be noted that when the switch was made from CFC 11 foam to HCFC 141b foam, a decrease in adhesion properties was observed. The HCFC 141b pour foam was dislodged from SRB plugs upon splashdown. The number of missing "plugs" was a cause for concern requiring process changes. Future material qualification programs will be expanded to mitigate the concerns associated with manufacturing processability problems and in-flight anomalies. These additional requirements will result in increased replacement costs relative to those associated with replacement of CFC 11 blown foams.

In summary, Shuttle material and process changes require extensive development and qualification programs prior to implementation. All of the information gained from the implementation of HCFC 141b is being utilized in the development of next-generation blowing agents. Lessons learned from implementation of HCFC 141b blown foams demonstrate that changes in materials and processes, even when thoroughly tested, present opportunities for unforeseen problems. Minimizing these issues is critical to the Shuttle program, and is part of what makes development of the next-generation TPS foams a lengthy and complex process.

## SPACE SHUTTLE PROGRAM PETITION FOR HCFC 141b Exemption Allowance

### 4.2 HCFC 141b REPLACEMENT EFFORTS

The Shuttle program began its efforts to eliminate the use of ODCs in foam in 1989. In 1992, EPA accelerated the phaseout of HCFC 141b from 2030 to 2003. Although the majority of resources were dedicated to the development and implementation of HCFC 141b foams to replace the class I ODCs, investigations into the next generation foams were also initiated at that time. HCFC 141b foams were implemented on the Shuttle elements in 1996 but continue to tie up resources with processing and in-flight problems. Specifically, two of the four ET foam systems had issues with processing and exhibited reduced flight performance associated with HCFC 141b. These resources were originally allocated for next generation foam development.

The polyurethane community has been fragmented in its development of HCFC 141b replacements. Patent rights, licensing agreements, and business decisions have complicated and slowed the availability of materials for scientific research and progress toward HCFC 141b replacement. SSP personnel have been driven to research a wide variety of replacement options. This research has included coordination with industry involving direct communication with numerous companies, such as Honeywell, Solvay, Exxon, Mobil, Bayer, 3M, Atofina, Halocarbon Products, PCR, and others. Transfer of foam replacement technology and exchange of successes, challenges, and disappointments in the search for blowing agent replacements continues with these companies and with our systems suppliers.

As part of the steps taken to find alternatives and share NASA developed technology, SSP team members have participated and presented data in more than 60 conferences or technical interchange meetings where they have worked with representatives of other companies in the area of alternative blowing agents. For example, results of SSP development work on HFC, HFE, and water-blown foams were presented at the Society of Plastics Industry Urethanes Conference and a NASA-sponsored conference on aerospace materials & environmental issues. Many different sources of blowing agent information have been utilized including: aerospace companies, NASA, military services, chemical companies, universities, libraries, national laboratories, and blowing agent manufacturing companies. Increased knowledge has come from technical interchange meetings, conference attendance, teleconferences, database services, teaching, and information provided by blowing agent manufacturers, and professional organizations. NASA is actively facilitating communication among those working on ODC replacement by holding regular technical interchange meetings with its subcontractors to address the development of the next generation of insulation foams. Research and development work is performed at NASA's Marshall Space Flight Center (MSFC) as well as Shuttle contractor sites. Efforts to ensure the continued availability of the Space Shuttle are of major concern and are directed by the Johnson Space Center (JSC).

Potential blowing agents that have been screened include the leading industry rigid foam candidates, HFC 245fa and pentane blends, as well as other hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs), hydrocarbons, and water as both a sole and co-blowing agent. The SSP has researched and tested over 200 potential blowing agent candidates.

More extensive tests, including simulated flight environments, have been conducted on TPS foams blown with HFCs, HFEs, hydrocarbons, and water. Limited test quantities and lack of availability have delayed development and qualification schedules of the HFCs and HFEs. For example, it was necessary to obtain HFC and HFE samples from specialty fluorine synthesis houses because test quantity samples of these materials were not available from the major manufacturers. Initial SSP efforts to obtain HFC 245fa from its sole manufacturer, Allied Signal (now Honeywell), were unsuccessful. Since mid-2000, limited HFC 245fa has been available for evaluation. HFC 245fa has been procured and testing is now in progress on HFC 245fa blown foams. Initial trials required significant processing adjustments to obtain acceptable foam properties.

HFE testing has also experienced delays and concerns. Safety issues associated with material flammability, low flash points, and limited toxicity data hindered progress. Some HFEs are used as commercial anesthetics and, thus, their toxicity characteristics are well established. However, because the Food and Drug Administration controls anesthetic use, they were not initially available in sufficient quantities for SSP screen testing. Limited quantities have now been obtained and are being used in foam spray trials.

The European community has moved to blowing agents that are blends of cyclopentane and isopentane. These blowing agents are classified as volatile organic compounds (VOCs) that may require emission controls under US state and federal clean air regulations. They are also flammable, and would require appropriate safety measures for use in spray and pour applications. However, they remain under consideration due to promising material

## SPACE SHUTTLE PROGRAM PETITION FOR HCFC 141b Exemption Allowance

property characteristics. Key characteristics and SSP concerns associated with potential blowing agent categories are summarized in Table 4.1.

Candidate	Results	Comments
Water/Carbon Dioxide (H <sub>2</sub> O/CO <sub>2</sub> )	<ul style="list-style-type: none"> <li>◆ Candidate for limited close-out applications</li> <li>◆ Requires substantial development for spray systems</li> <li>◆ Co-blowing required</li> </ul>	<ul style="list-style-type: none"> <li>◆ Currently used by industry in polyurethane foam systems</li> <li>◆ Unacceptable thermal conductivity for most SSP applications</li> <li>◆ Significant formulations modifications required</li> <li>◆ Reduced cryogenic strain compatibility</li> <li>◆ Water as a co-blowing agent is currently being evaluated in SSP performance tests</li> </ul>
Hydrofluorocarbons (HFCs)	<ul style="list-style-type: none"> <li>◆ Handling and process challenges due to low boiling point</li> <li>◆ Reduced Solubility</li> <li>◆ Good mechanical properties</li> <li>◆ Thermal testing and analysis in progress</li> </ul>	<ul style="list-style-type: none"> <li>◆ Require special handling equipment &amp; significant processing adjustments</li> <li>◆ Would require foam processing facility upgrades</li> <li>◆ Tradeoff between boiling point and solubility; those that are optimum for both are not easily manufactured, or will not be commercially available (HFC 245ca)</li> <li>◆ HFC 245fa is a commercial product and is currently being evaluated in SSP performance tests</li> <li>◆ Other HFCs are not commercially available due to licensing or patent issues.</li> </ul>
Hydrocarbons	<ul style="list-style-type: none"> <li>◆ Improved dimensional stability</li> <li>◆ Fine cell structure in rigid foam systems</li> <li>◆ Handling &amp; process challenges due to flammability</li> <li>◆ Limited data due to OSHA and NFPA imposed processing restrictions</li> </ul>	<ul style="list-style-type: none"> <li>◆ Requires special handling equipment and possible process adjustments</li> <li>◆ Would require foam processing facility upgrades</li> <li>◆ May require emission controls</li> <li>◆ Evaluations are planned</li> </ul>
Hydrofluoroethers (HFEs)	<ul style="list-style-type: none"> <li>◆ Excellent Thermodynamic properties</li> <li>◆ Compatible with existing chemical formulations</li> <li>◆ Limited data due to OSHA and FDA imposed restrictions</li> </ul>	<ul style="list-style-type: none"> <li>◆ High cost, but probably comparable to some HFCs</li> <li>◆ Limited toxicity data for some materials, extensive human and laboratory testing completed on other HFEs</li> <li>◆ Promising materials include commercial anesthetics, appreciable quantities have not been readily available for analysis</li> <li>◆ SSP is researching avenues for industry wide toxicology studies necessary to understand exposure limits, and any engineering controls that might be necessary to limit exposure.</li> <li>◆ Materials currently being evaluated in SSP performance tests</li> <li>◆ Would require foam processing facility upgrades</li> </ul>

*Table 4.1 Summary of Potential SSP Blowing Agent Replacements*

## SPACE SHUTTLE PROGRAM PETITION FOR HCFC 141b Exemption Allowance

NASA would like to take this opportunity to share with EPA a summary of SSP experience with candidate blowing agents to date.

### 4.2.1 Water/Carbon Dioxide (H<sub>2</sub>O/CO<sub>2</sub>)

Water reacts with the isocyanate component to produce both an amine catalyst and carbon dioxide by-products. The carbon dioxide acts as a blowing agent. The major concern with water blown foams is the high thermal conductivity of the carbon dioxide that resides within the cells of the urethane-based insulation. Water blown foams are typically used in applications where structural reinforcement is the primary purpose. Thermal insulations require blowing agents with much lower vapor phase thermal conductivity. In very limited cases on the SSP, the thermal conductivity is not the limiting design factor and a water blown insulation might have acceptable thermal conductivity, but the applications are few and it is not cost effective to qualify a water blown insulation at this time. The SSP is continuing the evaluation of water co-blowing to reduce the vapor pressures with HFC 245fa and reduce flammability of blended systems with pentane, but water as a sole blowing agent is not acceptable.

The various projects within the SSP report the following results. The SRB element investigated use of water blown foam insulation. A Product Research Corporation (PRC) material, PR822, was identified as a possible candidate. The pour foam produced had poor cell structure, as large voids caused the individual cells to collapse. The foam also had unacceptable density and strength properties. Other water blown foams tested also demonstrated an unacceptable inconsistency in cell formation. CO<sub>2</sub> was tested as a potential blowing agent by the Orbiter project but was rejected due to a number of factors. Thermal conductivity, compressive strength, adhesion and structure of CO<sub>2</sub> blown foam did not meet Orbiter requirements.

The ET project developed an in-house water blown insulation that had marginal thermal conductivity, but good dimensional stability. It passed cryogenic strain testing and had good performance in aerothermal recession testing. However, the auto-catalytic nature of the water blown reaction made the reaction too fast for a large portion of the ET applications. Additional formulation adjustments and specialized mixing and dispensing equipment would be required prior to qualification for the ET. The ET project is continuing the evaluation of water co-blowing with HFC 245fa, HFEs and pentane, but water as a sole blowing agent is not acceptable.

### 4.2.2 Hydrofluorocarbons

Limited studies have been performed with HFCs obtained from specialty blend houses, including HFC 245fa, HFC 356, HFC 365, HFC 245eb, and HFC 245ca. Some HFCs had acceptable boiling points, but low solubility in urethane components. Although the SSP considers several HFCs to be promising candidates, availability for testing has been limited due to patents and licensing agreements. The results of SSP evaluation of HFC 245fa follow.

HFC 245fa has a significantly lower boiling point than that of HCFC 141b. This has resulted in the need for equipment modifications, including pressurized cylinders and refrigerated storage. The vapor pressure has also dictated the need for modified blend vessels, blending procedures, and pumping and metering equipment that in turn have required significant adjustments prior to producing a material that can be sprayed for testing. The need for pressurized application equipment also necessitates more frequent maintenance of seals, valves and pressure regulators.

The gaseous nature of HFC 245fa at ambient conditions also presents challenges in foam formulation processes. Blending accuracy on a weight percentage basis is difficult, as the weight of the blend vessel fluctuates with internal pressures that rise as the gaseous blowing agent is added. To obtain blend accuracy required by the SSP, procedural changes are needed to vent and weigh the blend vessel in an iterative loop. Appreciable amounts of blowing agent are lost to the atmosphere during these cycles. This evaporative loss significantly affects specific gravity measurements that are critical to ensure accurate chemical stoichiometry.

Once blended, application of HFC 245fa blown foams requires significant process adjustments compared to current systems. The higher vapor pressure of HFC 245fa contributes to frothing, which complicates spraying and equipment flush procedures. Elevated feed pressures are required to preclude pump cavitation and inaccurate feed ratios. Spray gun modifications must be developed to optimize spray pattern distribution and minimize overspray. SSP foam is applied to large acreage with tight thickness tolerances necessary to meet design requirements. The design thickness requirements become more difficult to meet when using high vapor

## SPACE SHUTTLE PROGRAM PETITION FOR HCFC 141b Exemption Allowance

pressure blowing agents. The HFC 245fa comes out of solution with pressure spikes associated with rapid flow rate changes and causes unacceptable variations in foam thickness.

The exothermic chemical reaction of urethane insulations must be adjusted and tuned to accommodate changes in heat of reaction, vapor pressure of blowing agent, and solubility of blowing agent in both the liquid materials and reacting polymer. Proprietary formulation changes are necessary to achieve targeted densities, reaction profiles, and material properties. The surfactant package, catalysts, reactive polyol blend and isocyanate index must all be properly adjusted.

HFC 245fa has a significantly higher vapor pressure than HCFC 141b, which results in more overspray (material that accumulates on adjacent areas during spraying) during the warm-up and spray activities. This overspray, which is more porous than the overspray produced with HCFC 141b systems, tends to char and degrade, resulting in heat buildup and potential for fire. The SSP is aware of the dangers associated with exothermic reactions and heat build-up in urethane insulations. Precautions are taken to break up the foam over-spray material produced during processing to allow the heat it generates to dissipate. These precautions were not sufficient when handling experimental HFC 245fa blown foam blends, and fire resulted. The SSP has implemented special procedures to accommodate the safety concerns associated with fire protection, and we are again conducting evaluations with additional precautionary procedures.

Extensive testing within the SSP has been conducted on HFC 245fa blown spray foams. Preliminary data from an experiment conducted in 2001 show promise for spray foam applications, but significant processing changes were required. Adjustments were made to evaluate water co-blowing with HFC 245fa. Testing continues and analysis of the available data indicates promising results. Additional SSP performance tests are scheduled. HFC 245fa is not suitable for typical hand-mix and pour procedures used in SSP operations due to its low boiling point.

### 4.2.3 Hydrocarbons

Hydrocarbon blowing agents, most prominently pentane-based blowing agents, are VOCs and are significantly more flammable than HCFC 141b. It will be necessary to modify handling and processing equipment including electrical grounding systems, inert gas purges, extensive gas sensors to monitor for explosive limits, integration of the sensors with processing controls to ensure fail safe operations, and adequate exhaust systems to comply with National Fire Protection Agency standards. Use of Class I Division 1 explosion proof equipment and facilities are the only proven method to ensure safety and continued Space Shuttle production.

The flammable nature of pentanes also presents challenges in foam formulation processes. Blending of liquid components must now be accomplished in closed systems to prevent migration of flammable vapors.

Despite the challenges posed by their flammability and volatility, these materials exhibit promising characteristics. The hydrocarbons produce a very fine cell structure in rigid foam systems. They also provide foams with greater dimensional stability than HCFC 141b. The SSP will continue to evaluate hydrocarbon-based TPS foams.

### 4.2.4 Hydrofluoroethers

Many of the fluorinated ethers have optimal thermodynamic properties for use as a blowing agent in urethane insulations. Several materials have been evaluated for solubility and compatibility with the foaming reaction and found to be very promising. This research has been previously documented and data was presented at an EPA sponsored conference on CFC alternatives in 1992. One of the major concerns with the experimental ethers was the lack of toxicity data and sporadic reports of instability. In the case of HCFC 141b development, industry pooled resources and jointly funded the toxicity, stability and compatibility testing. Industry has not yet collaborated on the development of data for any next generation HFE blowing agent.

Both HFE 245 and HFE 263 were tested for SSP use. These materials have blowing efficiencies comparable to current SSP blowing agents. They were also found to have sufficient solubility in foam components, and produce a foam with low thermal conductivity. Preliminary data also indicated acceptable mechanical/physical properties in molding and sprayed systems. Unfortunately, both HFE 245 and 263 have limited toxicity data and are not commercially available, although HFE 245 is a pharmaceutical by-product. Further research into commercially available anesthetics led the SSP to discover several materials with appropriate boiling points for potential use as foaming agents in cellular polymeric insulations. This class of materials appears extremely promising as potential blowing agents. The SSP conducted spray trials with representatives of industry and the EPA in

## **SPACE SHUTTLE PROGRAM PETITION FOR HCFC 141b Exemption Allowance**

attendance. Tests of foam properties were acceptable and the SSP is currently seeking the means to obtain larger test quantities of these materials for continued evaluation in performance tests.

### **4.3 FUTURE HCFC 141b REPLACEMENT PLANS**

NASA supports EPA's Significant New Alternatives Program, which strives for the substitution of chemicals that reduce overall risks to human health and the environment. However, the critical path to blowing agent selection, evaluation, qualification, and final implementation in a human-rated propulsion system is complex, lengthy, and expensive. Considerable effort and resources have been spent on replacing HCFC 141b foam systems, without success. The SSP has expanded its list of candidates to include custom-developed materials and blowing agent blends. Candidate considerations include not only those of the SSP, but also those of potential future launch vehicles. Successful completion of TPS replacement in the timeframe outlined below is contingent on identification of viable alternative blowing agents. It is possible that additional time may be required.

#### **4.3.1 FY 2001 – FY 2003**

The SSP will continue to build on past efforts to replace HCFC 141b. We will expand our list of candidates, testing a wide range of blowing agents, blowing agent combinations, and foam formulations. Design of multiple experiments and testing permutations will be required to capture the necessary data. Formulations are tested by spraying them on numerous sub-scale test panels. NASA is also in the process of upgrading MSFC facilities to accommodate safe testing of flammable blowing agents. Several next generation materials have shown promise, but with significant adjustments required. HFC, HFE and water blown formulations are currently undergoing processing evaluations and extensive performance tests that are required prior to flight qualification tests.

The SSP is also investigating in-house foam development. A small-scale blend facility is being installed at MSFC to support in-house development of next generation formulations. Spray and pour foam formulations are being developed and their properties evaluated. The culmination of this development program will be candidates suitable for further assessment.

#### **4.3.2 FY 2003 – FY 2006**

Once candidates have been downselected, the information collected in the first stage of testing will be used to develop optimized processes for each material. After spray optimization, an extensive test program will be initiated to gather data needed to populate the engineering database for each candidate. This database will include information acquired from lot-to-lot evaluations, thermal testing, mechanical property testing, performance testing, and wet chemistry analyses. Test sprays will be performed on panels and test articles and will include production-type duration sprays. Final selections of alternate foam systems will be made at the end of this test period. Upgrades for production spray cells for the final next generation materials will be identified and initiated at this time.

#### **4.3.3 FY 2006 – FY 2010**

Production upgrades and material qualification must be completed before next generation TPS materials may be implemented. For example, "confidence" sprays of two ET mockups in production cells must be successfully completed before a next generation TPS may be used on flight hardware. Test articles are sprayed and tested to collect information required to populate the flight database for each foam.

Historically this process has taken 4-6 years. NASA is diligently working to implement zero ODP replacement TPS on the Shuttle system by FY 2010.

Blowing agent replacement is technically complex, and the changes involve significant program implementation risk. The next-generation blowing agents represent a much greater technical challenge and programmatic risk than the development and implementation of HCFC 141b. Foams made with alternate blowing agents meeting Shuttle criteria are not yet available, so the transition from HCFC 141b to a zero ozone depleting potential (ODP) blowing agent cannot be accomplished within the existing phaseout timelines without jeopardizing the safety of NASA's human space flight program.

# SPACE SHUTTLE PROGRAM PETITION FOR HCFC 141b Exemption Allowance

## 5.0 OTHER SOURCES OF HCFC 141b

The use of stockpiled, recycled or recovered supplies of HCFC 141b as the sole source of foam blowing agent through the time anticipated to implement next generation foams poses unacceptable risk to the Shuttle Program. The stability and purity of the blowing agent is essential to viable foam insulation meeting the stringent technical requirements of manned flight hardware.

Time for implementation, uncertainties in long-term quality of stored, recycled or recovered HCFC 141b, and logistical issues make such options appropriate only as contingencies for continued SSP viability. Some candidate blowing agents will not be commercialized until close to the January 2003 class II phaseout date, delaying final material selection. The qualification effort to validate and implement a new blowing agent in such critical space vehicle applications has historically taken four to five years after the blowing agent has been selected. Development, qualification and implementation of next generation foams are accomplished through an iterative process during which unanticipated challenges may require changes to, modification of, or replacement of equipment, delivery methods, and other parameters. These types of changes may extend the time for full implementation of replacement insulative foams. Additional time will also be required to incorporate lessons learned from efforts associated with the implementation of HCFC 141b blown foams. Considering these additional time requirements, qualification and implementation of replacement foams is expected to be complete no earlier than 2009.

The use of recycled or recovered supplies would be counterproductive. A change in the source of any critical ingredient automatically triggers requalification requirements. The SSP has requalification requirements for flight-essential formulations that would result in years of testing and waste of resources. These requirements reflect the element of human risk involved in manned space flight.

The Shuttle Program does not yet have sufficient data to be assured of long-term stability of stored HCFC 141b. In November 1999, the ET project initiated a study to determine HCFC 141b shelf life. Data suggests that HCFC 141b should be stable at least 2 years in storage under ambient factory conditions. Manufacturers are unwilling to certify that the material will not chemically decompose or degrade if stored through 2009, even if a chemical stabilizer is added. HCFC 141b used in SSP insulating foams does not incorporate a stabilizer. The manufacturer's testing has demonstrated storage stability under normal conditions only for up to one year, far short of the minimum eight years required for Shuttle system support.

Long-term cyclic effects on aged blowing agent purity are unknown. The unresolved storage concerns include the effect of storage conditions such as container material, temperature, atmosphere, humidity control, and the effect of degradation products on the stability. Two potential problem schemes exist. The principal problem is that the accumulation of degradation products may have an irreversibly deleterious effect upon the foam's thermal conductivity. Second, if the deleterious effect of degradation products is not irreversible and can be remedied with chemical reprocessing, ultimate reprocessing success would still need to be established. Reductions in blowing agent purity level due to degradation by-products or the introduction of impurities from the storage vessel itself may adversely affect the performance of the TPS. Loss of the TPS would bring the SSP to a halt.

The SSP annual requirement for HCFC 141b is anticipated to be approximately 40,000 lbs (18,000 kg). Assuming successful implementation of replacement TPS by the earliest possible date, 2009, over 280,000 lbs (126,000 kg) must be stored to ensure adequate supply of HCFC 141b. Storage of such a large amount of HCFC 141b in drums or railcars would create the potential for material contamination, spills, emissions, and material management issues. The need to stockpile such large quantities for the length of time anticipated for next generation foam development could result in a significant disposal requirement at the time of implementation. Further, there is a risk that even this large amount of material could be insufficient for Shuttle requirements. If initial replacement blowing agent choices fail qualification testing, development work would have to be restarted with other candidate blowing agents, extending the total time to implementation.

Foam insulation is critical to flight and mission success. Using recycled, recovered, or stockpiled HCFC 141b as the future blowing agent source poses unacceptable environmental and material availability risks to the Shuttle Program. Continued production and availability of HCFC 141b past 2002 is necessary to meet the stringent requirements of SSP foam insulation.

## SPACE SHUTTLE PROGRAM PETITION FOR HCFC 141b Exemption Allowance

### 6.0 CLEAN AIR ACT COMPLIANCE

Production of HCFC 141b past 2002 for space vehicles does not conflict with the requirements of the Clean Air Act (CAA). Section 606(a) of the CAA as amended in 1990 provides the EPA Administrator with authority to accelerate the phaseout of ozone-depleting substances. EPA has accelerated the phaseout of class II ODCs relative to the requirements of the Montreal Protocol phaseout schedule. This accelerated date is reasonable for those applications for which acceptable substitute materials are available. The SSP, however, has identified no acceptable alternative to HCFC 141b in thermal protection foam applications.

EPA established an accelerated schedule for the phaseout of HCFC 141b on December 10, 1993, 58 FR 65018, based on CAA sections 606(a)(1) and 606(a)(2). The preamble for this action states, "...EPA believes it has the authority to take into account the technological achievability of a specific schedule in accelerating a phaseout schedule on the basis of scientific findings. Congress itself recognized the linkage between the need to phaseout the production and consumption of ozone-depleting chemicals to protect the environment and human health and the availability of substitutes for those chemicals".

At that time, EPA believed that research into alternatives, "particularly for HCFC 141b in foam... is currently ongoing and should result in the availability of substitutes by the dates contained on the HCFC phaseout schedule." Replacements are available for many foam applications. However, there is nothing commercially available today that meets the stringent requirements of human-rated space flight.

In the same Federal Register, EPA also stated, "the Agency believes that the use of HCFCs should be limited to only those applications where other environmentally acceptable alternatives do not exist". It is no longer practicable to accelerate the phaseout of HCFC 141b for space vehicles. EPA has the authority under Section 606 of the Act to promulgate exceptions to the accelerated schedule and to consider "other relevant factors" (606(a)(2)). An exception to the accelerated phaseout is allowable and in compliance with applicable laws and statutes.

## SPACE SHUTTLE PROGRAM PETITION FOR HCFC 141b Exemption Allowance

### 7.0 CONCLUSION

The Space Shuttle Program requires a thermal protection system to maintain the quality of the cryogenic propellants, provide protection from aerothermal and vehicle plume heating environments, prevent formation of ice on exterior surfaces, and maintain structural integrity. The TPS is rigid foam using HCFC 141b as the chemical blowing agent to provide the critical insulation and cell structure properties. Development and implementation of an HCFC 141b replacement cannot meet the 2003 deadline. The SSP began HCFC 141b replacement efforts far in advance of the phaseout, but no replacement has been found that meets performance requirements. Stockpiling or use of recycled or recovered HCFC 141b is not a viable long-term solution due to shelf life and environmental concerns. Because Shuttle viability depends on continued production of HCFC 141b for use as a foam blowing agent past January 1, 2003, EPA approval of NASA's petition for an HCFC 141b Exemption Allowance is critical to the NASA Space Shuttle Program.